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(54) BARIUM TITANATE-BASED SEMICONDUCTOR PORCELAIN COMPOSITION AND PRODUCTION THEREOF

(57)Abstract:
PURPOSE: To produce the barium titanate-based semiconductor porcelain composition low in specific resistance at a temp. and high in dielectric breakdown voltage by mixing the barium carbonate powder and the titanium oxide powder having a specified grain size and firing the mixture under an oxidizing atmosphere.
CONSTITUTION: The barium carbonate powder having 0.5-1.4μm average grain size and the titanium oxide powder having 0.5-1.1μm average grain size are prepared as an essential elements. This barium carbonate powder and this titanium oxide powder are mixed, and fired under an oxidizing atmosphere, and the objective composition is obtained. When these are mixed, an anionic org. dispersant is preferably added. Moreover, it is preferable that a part of the barium is replaced with stronitium and calcium, and at last one kind of element selected from among Bi, Nb, W, Ta and rare earth elements and manganese are added, and moreover, the solution phase generating component such as SiO2 and TiO2 is added as the accelerated for semiconductor.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention shows a property forward in the temperature coefficient of electric resistance and the specific resistance in a room temperature is small related with a barium titanate system semi-conductor porcelain constituent with a big breakdown voltage.
[0002]
[Description of the Prior Art] It is known that the barium titanate system semi-conductor porcelain constituent (henceforth a PTC constituent) which has a steep forward resistance temperature characteristic in barium titanate conventionally by carrying out minute amount addition of a semi-conductor-ized agent, for example, Bi and Nb, W, and Sb, or the rare earth metal when near the temperature of the Curie point which specific resistance is small and is phase transition point is crossed near a room temperature will be obtained.
[0003] Such a PTC constituent is used for the constant temperature heating element, a component for automatic demagnetization or a current-limiting component of color television, etc. using the steep forward resistance temperat characteristic.
[0004] It is mentioned that forward resistance rate of change when the specific resistance in a room temperature generally crosses a small thing and near the temperature of the Curie point as a property for which the PTC constitue for current-limiting components is asked is large, and that dielectric breakdown voltage is high.
[0005] Although mostly proposed from the former about a PTC constituent and its manufacture approach, in any cas what has the small specific resistance in a room temperature had low dielectric breakdown voltage, and, on the other hand, as for what has high dielectric breakdown voltage, the specific resistance in a room temperature was large. Tha is, as for the thing of 5 ohm-cm, dielectric breakdown voltage is set to mm in about 20-30v /by the specific resistanc the time of a room temperature, on the other hand, dielectric breakdown voltage is set to mm in about 40-60v /by the specific resistance at the time of a room temperature, and the things of 10 ohm-cm are these. When seen by the index ratio (VBD/rho) of dielectric breakdown voltage (VBD) and the specific resistance (rho) at the time of a room temperature, in any case, it became less than [4-6, or it], and the above-mentioned index ratio lacked [case / dielect breakdown voltage] in practicality small considering specific resistance.
[0006] Then, the PTC constituent indicated by JP,5-51254,A is known as that in which the specific resistance at the time of a room temperature has the property that the above-mentioned index ratio exceeds 6, by less than 10 ohm-cm By using BaTiO3 as a base constituent, 4 - 15 mol% is done for Sr, it does the 3-12 mol% permutation of 13 - 18 mo and Pb for calcium, and the above-mentioned PTC constituent is 0.15-0.5-mol% and Mn about semi-conductor-ized agents, such as rare earth elements, such as Y, and Nb, Bi. 0.002-0.025-mol% and SiO2 It adds so that it may becom 0.2-0.7-mol%.
[0007] Moreover, the PTC constituent indicated by JP,5-70223,A is known as what has the aforementioned property The above-mentioned PTC constituent uses BaTiO3 as a base constituent, does the 1 mol% permutation of 15 - 20 mol% and Pb for calcium, and is Nb 2O5 as a semi-conductor-ized agent. 0.1-0.18mol % and Mn 0.07 - 0.10 mol% a SiO2 It adds so that it may become 2.5-5.0-mol%.
[0008] However, with each above-mentioned PTC constituent, the problem is produced by containing Pb which has toxicity in respect of the problem over the environment on industry, i.e., the problem of waste treatment, and the hea care of the worker engaged in production.
[0009] Then, lead (Pb) is removed from those presentations about sample No.2 indicated by JP,5-70223,A in order to avoid the above-mentioned problem, and sample No.6, and they are each sample No.2' and sample No.6'. It prepared
[0010] However, in order to raise a moldability, it is necessary to consist of a zirconium dioxide (ZrO2), to cover, an to cover baking metal mold with powder, and they are above-mentioned sample No.2' and sample No.6'. When burn temperature was made into 1340 degrees C, it covered the account of a top and the fault of having reacted with powd and forming high resistance was produced. Furthermore, although the above-mentioned burning temperature was

prepared as 1300 degrees C, the reaction was seen similarly and fault was produced.
[0011] Then, the following results were brought when the above-mentioned burning temperature was prepared at 128 degrees C. In sample No.2', specific resistance (ohm-cm) is set to 4.31, dielectric breakdown voltage (v/mm) is set to 32.11, VB.D / rho which is the ratio of dielectric breakdown voltage and specific resistance are 7.52, at sample No.6 specific resistance (ohm-cm) is 5.51 and dielectric breakdown voltage (v/mm) is 43.52. It became and VB.D / rho wa 7.90.
[0012]
[Problem(s) to be Solved by the Invention] However, each sample No.2' and No.6' which excluded lead as mentione above Although specific resistance was low resistance comparatively then, VB.D / rho which dielectric breakdown voltage becomes low and becomes an index for miniaturizing each above-mentioned sample became high. For this reason, the above-mentioned each sample No.2' and No.6' If it uses for a constant temperature heating element, a component for automatic demagnetization or a current-limiting component of color television, etc. as mentioned abo high dielectric breakdown voltage and the problem of inviting enlargement in order to secure low resistance are produced.
[0013]
[Means for Solving the Problem] The barium titanate system semi-conductor porcelain constituent of this invention according to claim 1 is a mean diameter in order to solve the above technical problem. 0.5-1.4 Barium-carbonate powder of mum, and mean diameter 0.5-1.1 The titanium oxide powder of mum is used as a main raw material, the above-mentioned barium-carbonate powder and titanium oxide powder are mixed, and it is characterized by being calcinated under an oxidizing atmosphere.
[0014] An anionic organic system dispersant is added to the combination constituent which uses barium-carbonate powder and titanium oxide powder as a principal component, the above-mentioned combination constituent is mixed and the manufacture approach of the barium titanate system semi-conductor porcelain constituent of this invention according to claim 2 is characterized by being calcinated under an oxidizing atmosphere.
[0015] The barium titanate system semi-conductor porcelain constituent of this invention according to claim 3 In the barium titanate system semi-conductor porcelain constituent with which it is mixed and the barium-carbonate powde and titanium oxide powder as a main raw material are calcinated under an oxidizing atmosphere The strontium (Sr) atom of 1 - 10 mol% and the calcium (calcium) atom of 13 - 18 mol% are permuted to the barium (Ba) atom of the above-mentioned barium carbonate. At least one sort of elements among Bi, Nb, W, Ta, or rare earth elements as a semi-conductor-ized agent Furthermore, 0.22 - 0.35 mol%, As opposed to the base constituent which contains 0.05 - 0.10 mol% for manganese (Mn) Furthermore, liquid phase generation component containing a silicon dioxide (SiO_2 and titanium oxide (TiO_2) 1.5-3.2 It contains in the range of mol%. And content of the above-mentioned silicon dioxide It is 0.3-2.3-mol% of within the limits, and the above-mentioned barium-carbonate powder is a mean diamet 0.5-1.4 It is mum and the above-mentioned titanium oxide powder is a mean diameter. 0.5-1.1 It is characterized by being mum.
[0016] The above-mentioned barium carbonate is mean particle diameter. 0.5-1.4 Although it will not be especially limited if it is mum, carry out elevated-temperature reduction of what mixed with oil coke or an anthracite to homogeneity the baryte ($BaSO_4$) ground well, consider as a water-soluble barium sulfide, refine this barium sulfide, the water solution of the approach to which that water solution is made to react with a sodium carbonate water soluti or the refined above-mentioned barium sulfide is made to absorb carbon dioxide gas, and it is obtained.
[0017] The above-mentioned titanium oxide is a mean diameter. 0.5-1.1 Although it will not be especially limited if is with mum, the refined titanium tetrachloride is hydrolyzed in oxygen and hydrogen flame by the gaseous phase, it obtained, and there is neither water of crystallization nor attached groundwater. In addition, the ratio of the mean particle diameter of the above-mentioned barium carbonate and titanium oxide has desirable within the limits of 0.5- in order to maintain miscibility good. In addition, each above-mentioned mean particle diameter was measured by th Coulter counter method.
[0018] As the above-mentioned organic system dispersant, in order to avoid condensation of barium-carbonate powd and titanium oxide powder, in consideration of ionicity, an anionic organic system dispersant is desirable. Moreover although it has the effectiveness that the organic system dispersant of the Nonion system also avoids condensation, a more nearly anionic organic system dispersant is not remarkable. In addition, oxidative degradation of it is carried ou and the above-mentioned organic system dispersant disappears, when it calcinates under an oxidizing atmosphere.
[0019] Moreover, wet blending of the compound with which the barium carbonate etc. was blended was carried out, and after filtration desiccation, the bottom of an oxidizing atmosphere, and after carrying out temporary quenching a 1000-1200 degrees C for 1 to 5 hours and pulverizing the compound after temporary quenching, it was made into the shape of a slurry in BAIDA, and carried out granulation desiccation. Then, it is at 1300-1380 degrees C under an oxidizing atmosphere about the above-mentioned mold goods after fabricating, a granulation object in a predetermine configuration and obtaining mold goods. It calcinated for 0.1 to 3 hours, and the burned product of a barium titanate

system semi-conductor porcelain constituent was obtained.
[0020] When the amount which permutes the location of the above-mentioned Ba atom by calcium atom becomes under 13 mol%, it becomes impossible to maintain dielectric breakdown voltage highly, and the particle which constitutes the organization of the constituent obtained when 18 mol% was exceeded makes it detailed, and specific resistance becomes large. Furthermore, it can be set as the Curie point temperature in the case of using as for exampl a current-limiting component by setting up the amount which permutes the location of the above-mentioned Ba atom by Sr atom within the limits of 1 - 10 mol%. Moreover, the amount of permutations of the above-mentioned Sr atom can raise the melting point of the obtained constituent.
[0021] Moreover, under by 0.22 mol%, gradually, if specific resistance becomes large and 0.35 mol% is exceeded, a for the addition of a semi-conductor-ized agent, specific resistance will become large rapidly.
[0022] Liquid phase generation component If the specific resistance of the constituent obtained when the 1.5-3.2-mo range of % was crossed becomes large and exceeds especially 3.2-mol%, the zirconium dioxide (ZrO2) which becom fault sintering and is used in the case of baking will cover, and it will react with powder. Moreover, when it comes to under 0.3 mol %, the addition of a silicon dioxide promotes the rearrangement of the effectiveness as a liquid phase generation component, i.e., the particle at the time of baking, extreme abnormality particle growth is controlled, the effectiveness of mitigating the fall of dielectric breakdown voltage becomes low, and on the other hand, if 2.3-mol% exceeded, dielectric breakdown voltage will become low to the specific resistance at the time of a room temperature.
[0023] Furthermore, it becomes unsuitable, in case the constituent obtained when specific resistance would become large extremely, if forward temperature resistance rate of change will become small if, as for Mn, the addition becom under 0.05 mol%, and the addition of Mn exceeded 0.10 mol% on the other hand is used as for example, a current-limiting component.
[0024]
[Example] It will be as follows if one example of this invention is explained. In the barium titanate system semi-conductor porcelain constituent, barium-carbonate powder and titanium oxide powder are used as a main raw materi and the quality of a liquid phase product is mixed and calcinated by the Curie point migration matter to which a bariu site is permuted and Curie point temperature is moved, a semi-conductor-ized agent and a mineralizer, and the pan to the above-mentioned main raw material.
[0025] At this time, it is the mean diameter of the above-mentioned barium carbonate, and 0.5-1.4. mum and mean diameter of the above-mentioned titanium oxide 0.5-1.1 It is set as mum. In addition, the above-mentioned mean particle diameter was measured by the Coulter counter method. Moreover, an organic system dispersant (the Dai-Ich Kogyo Seiyaku Co., Ltd. make, SERAMO D-134) anionic to the time of mixing with the above-mentioned main raw material and other combination constituents is 0.1-0.8. Weight % use of is done.
[0026] A strontium carbonate (SrCO3) is used as Curie point migration matter among the above-mentioned combination constituents, and the above-mentioned strontium is for moving Curie point temperature for the barium s of the obtained barium titanate system semi-conductor porcelain constituent to a low temperature side by the permutation.
[0027] as the above-mentioned semi-conductor-ized agent -- as oxidization neodium (Nd 2O3) and a mineralizer -- a manganese carbonate (MnCO3) and calcium -- a calcium carbonate (CaCO3) -- using -- as the above-mentioned qua of a liquid phase product -- a silicon dioxide (SiO2) -- superfluous -- a part -- titanium oxide (TiO2) It used.
[0028] Although addition of the above-mentioned superfluous titanium oxide is generally blended so that a titanium atom may serve as equimolar to a barium atom, it says that many, i.e., superfluously, mol loadings of a titanium atom are blended from the number of combination mols of a barium atom. Therefore, in this invention, it is set up so that t mol loadings of a titanium atom may become superfluous to the combination molar quantity which the barium atom, the strontium atom, and the calcium atom totaled.
[0029] Next, when the above-mentioned barium titanate system semi-conductor porcelain constituent is explained in more detail, it is, As a fine-particles raw material, the barium carbonate of a high grade (BaCO3) (mean particle diameter of 1.34 micrometers), Titanium oxide (TiO2), a strontium carbonate (SrCO3) (0.85 micrometers of mean diameters), and oxidization neodium (Nd 2O3) (mean diameter 1.5 micrometers), (1.07 micrometers of mean diameters) It blends, respectively so that it may become the presentation ratio which indicated manganese carbonate (MnCO3) (mean particle diameter 5.2 micrometers) and a silicon dioxide (SiO2) to Table 1 and 2. (mean particle diameter 4.0 micrometers) With the iron ball which carried out nylon coating with ion exchange water or distilled water, it supplied in the ball mill and wet blending was carried out for 24 hours.
[0030]
[Table 1]

原料 / 試料No.	$BaCO_3$	$SrCO_3$	$CaCO_3$	TiO_2	Nd_2O_3	$MnCO_3$	SiO_2
＊1	79.74	5	15	100.0	0.13	0.08	0.5
2	79.74	5	15	100.5	0.13	0.08	1.0
3	79.74	5	15	100.5	0.13	0.08	1.5
4	79.74	5	15	100.5	0.13	0.08	2.0
5	79.74	5	15	100.5	0.13	0.08	2.5
6	79.74	5	15	100.5	0.13	0.08	0.5
7	79.74	5	15	100.5	0.13	0.08	1.0
8	79.74	5	15	100.5	0.13	0.08	1.5
9	79.74	5	15	100.5	0.13	0.08	2.0
＊ 10	79.74	5	15	100.5	0.13	0.08	2.5
11	79.74	5	15	100.8	0.13	0.08	0.5
12	79.74	5	15	100.8	0.13	0.08	1.0
13	79.74	5	15	100.8	0.13	0.08	1.5
14	79.74	5	15	100.8	0.13	0.08	2.0
＊ 15	79.74	5	15	100.8	0.13	0.08	2.5
16	79.74	5	15	101.0	0.13	0.08	0.5
17	79.74	5	15	101.0	0.13	0.08	1.0
18	79.74	5	15	101.0	0.13	0.08	1.5
19	79.74	5	15	101.0	0.13	0.08	2.0
＊ 20	79.74	5	15	101.0	0.13	0.08	2.5
21	79.74	5	15	101.2	0.13	0.08	0.5
22	79.74	5	15	101.2	0.13	0.08	1.0
23	79.74	5	15	101.2	0.13	0.08	1.5
24	79.74	5	15	101.2	0.13	0.08	2.0
＊ 25	79.74	5	15	101.2	0.13	0.08	2.5
26	79.74	5	15	101.5	0.13	0.08	0.5
27	79.74	5	15	101.5	0.13	0.08	1.0
28	79.74	5	15	101.5	0.13	0.08	1.5
29	79.74	5	15	101.5	0.13	0.08	2.0
＊ 30	79.74	5	15	101.5	0.13	0.08	2.5
31	79.74	5	15	102.0	0.13	0.08	0.5
32	79.74	5	15	102.0	0.13	0.08	1.0
33	79.74	5	15	102.0	0.13	0.08	1.5
＊ 34	79.74	5	15	102.0	0.13	0.08	2.0
＊ 35	79.74	5	15	102.0	0.13	0.08	2.5

なお、上記原料の配合量は、モル%で示した。

[0031]
[Table 2]

原料 / 試料No.	$BaCO_3$	$SrCO_3$	$CaCO_3$	TiO_2	Nd_2O_3	$MnCO_3$	SiO_2
36	83.74	1	15	100.8	0.13	0.05	0.5
37	79.74	5	15	100.8	0.13	0.05	0.5
38	74.74	10	15	100.8	0.13	0.05	0.5
＊ 39	69.74	15	15	100.8	0.13	0.05	0.5
＊ 40	84.74	5	10	100.8	0.13	0.05	0.5
41	81.74	5	13	100.8	0.13	0.05	0.5
42	76.74	5	18	100.8	0.13	0.05	0.5
＊ 43	74.74	5	20	100.8	0.13	0.05	0.5
44	79.74	5	15	100.8	0.13	0.08	0.5
45	79.74	5	15	100.8	0.13	0.10	0.5
＊ 46	79.74	5	15	100.8	0.13	0.12	0.5
47	79.74	5	15	100.8	0.13	0.08	1.0
48	79.74	5	15	100.8	0.13	0.08	1.5
49	79.74	5	15	100.8	0.13	0.08	2.0
＊ 50	79.74	5	15	100.8	0.13	0.08	2.5
51	79.74	5	15	100.8	0.13	0.08	0.5
52	79.78	5	15	100.8	0.11	0.08	0.5
53	79.76	5	15	100.8	0.12	0.08	0.5
54	79.72	5	15	100.8	0.14	0.08	0.5
＊ 55	79.74	5	15	100.0	0.13	0.08	0.5

なお、上記原料の配合量は、モル%で示した。

[0032] Then, filtration desiccation was carried out and temporary quenching was carried out at the temperature of 1000-1200 degrees C under the oxidizing atmosphere for 1 to 5 hours. After obtaining the temporary-quenching pulverized coal which pulverized the sample after temporary quenching so that it might become the mean particle

diameter of 2 micrometers or less, the temporary-quenching pulverized coal was kneaded with the binder water solution which contains polyvinyl alcohol (PVA) 2% of the weight, it considered as the slurry, granulation desiccatio of the slurry was carried out with the spray dryer, and the granulation object was acquired.

[0033] About the above-mentioned granulation object, 1.0t /is [cm] the pressure of 2, for example, they are the diameter of 12.5mm, and thickness. It fabricated to 1.2mm discoid and mold goods were obtained. The mold goods a put in a baking sheath, a temperature up is carried out with the programming rate of 3 degrees C / min with an electri furnace, and it is at 1360 degrees C under an oxidizing atmosphere. After calcinating for 0.5 hours, the temperature w lowered by 3 degrees C / min, and each sample (No.1-55) from which the presentation ratio of each raw material diff was produced, respectively. In addition, when putting the above-mentioned mold goods in a baking sheath, it covere for raising the mold-release characteristic after baking, and the powder of a zirconium dioxide (ZrO_2) was used as powder.

[0034] Moreover, sample No.11 shown in Table 1 It blended, respectively in the combination of each mean particle diameter which replaced with the mean particle diameter of the barium carbonate used for the sample above, and titanium oxide, and was indicated to Table 3 and 4 about the thing of a presentation ratio, and the sample (No.56-72) was produced, respectively. In addition, sample No.11 were indicated again for convenience.

[0035]

[Table 3]

焼成温度1340℃

$BaCO_3$ \ TiO_2	1.07	0.89	0.60 μm
1.34 μm	試料No. (56)	(57)	(58)
1.04	(59)	(60)	(61)
0.60	(62)	(63)	(64)

[0036]

[Table 4]

焼成温度1360℃

$BaCO_3$ \ TiO_2	1.07	0.89	0.60 μm
1.34 μm	試料No. (11)	(65)	(66)
1.04	(67)	(68)	(69)
0.60	(70)	(71)	(72)

[0037] Each sample obtained as mentioned above is the diameter of 10.3mm, and thickness. It was 1.0mm discoid, a the silver paste of ohmic nature and the silver paste for covering could be burned on the both sides, the electrode was formed, and room temperature specific resistance, the Curie point, and dielectric breakdown voltage were measured, respectively. Those results were shown in Table 5 thru/or 7.

[0038]

[Table 5]

物性 / 試料No.	キュリー点 (℃)	比抵抗 (Ω・cm)	破壊電圧 (V/mm)	指標比 (V_{BD}/ρ)
* 1	108	14.49	79.41	5.48
2	106	8.11	57.26	7.06
3	107	7.45	61.16	8.21
4	107	7.22	67.43	9.34
5	109	6.84	67.10	9.81
6	106	6.81	51.96	7.63
7	104	5.35	47.13	8.81
8	104	4.65	43.90	9.44
9	101	5.52	56.30	10.20
* 10	105	6.74	43.74	6.49
11	102	4.60	49.36	10.73
12	106	4.03	36.96	9.17
13	107	3.65	36.65	10.04
14	106	4.34	42.62	9.82
* 15	102	7.22	34.08	4.72
16	105	4.60	49.36	10.73
17	106	3.82	45.04	11.79
18	105	4.34	50.30	11.59
19	104	4.03	42.19	10.47
* 20	101	6.38	28.77	4.51
21	103	4.99	50.55	10.13
22	106	3.99	46.36	11.62
23	106	3.70	40.59	10.97
24	105	3.65	38.80	10.63
* 25	※	※	※	※
26	103	7.95	74.97	9.43
27	107	4.24	44.86	10.58
28	108	4.57	43.14	9.44
29	107	4.66	33.88	7.27
* 30	※	※	※	※
31	102	8.82	63.06	7.15
32	103	5.72	48.45	8.47
33	107	5.61	42.97	7.66
* 34	※	※	※	※
* 35	※	※	※	※

※は、成形品の焼成時に、上記成形品が敷き粉のZrO_2と反応するため、成形不良となり、諸物性値が測定不能であることを示す。

[0039]
[Table 6]

物性 / 試料No.	キュリー点 (℃)	比抵抗 (Ω・cm)	破壊電圧 (V/mm)	指標比 (V_{BD}/ρ)
36	121	3.82	32.16	8.42
37	103	4.46	45.24	10.14
38	92	5.78	52.08	9.01
* 39	62	23.61	150.63	6.38
* 40	108	3.94	23.01	5.84
41	105	3.78	34.40	9.10
42	101	8.07	67.22	8.33
* 43	104	24.16	122.01	5.05
44	102	4.60	49.36	10.73
45	101	8.37	82.44	9.85
* 46	106	18.03	115.75	6.42
47	105	4.03	36.96	9.17
48	103	3.65	36.65	10.04
49	103	4.34	42.62	9.82
* 50	109	7.22	34.08	4.72
51	107	4.83	47.91	9.92
52	105	5.02	49.00	9.76
53	103	4.99	46.86	9.39
54	104	7.48	60.59	8.10
* 55	109	14.49	79.41	5.48

[0040]
[Table 7]

物性 / 試料No.	キュリー点 (℃)	比抵抗 (Ω・cm)	破壊電圧 (V/mm)	指標比 (V_{BD}/ρ)
56	107	4.83	47.91	9.92
57	103	4.47	43.27	9.68
58	103	4.98	46.36	9.31
59	102	5.34	58.21	10.90
60	106	5.02	54.42	10.84
61	101	4.05	42.93	10.60
62	105	6.75	57.24	8.48
63	100	4.84	51.59	10.66
64	103	4.18	48.86	11.69
11	102	4.60	49.36	10.73
65	102	4.68	48.81	10.43
66	104	4.85	49.91	10.29
67	101	5.66	66.90	11.82
68	101	5.22	61.07	11.34
69	103	4.54	51.48	11.34
70	105	7.14	66.19	9.27
71	101	4.97	56.71	11.41
72	102	4.61	57.07	12.38

[0041] Each sample of * mark in the above-mentioned table 1 and Table 2, 5, and 6 shows out of range [out of range of this invention], i.e., each example of reference, and each of other samples of all show each example which is with the limits of this invention. The PTC component of each example is increasing sharply [dielectric breakdown voltage /v / // mm and / 35-70] at the same time it has formed it into low resistance with 4 - 9 ohm-cm compared wi the thing of the example of reference, so that clearly from Table 5 thru/or 7. Equivalent [to the sample in which the index ratio (VBD/rho) of dielectric breakdown voltage (VBD) and the specific resistance (rho) at the time of a room temperature excluded and prepared lead from the constituent known conventionally] or it has become seven or more [beyond it].

[0042] Thus, this invention persons exclude the leaden addition which has toxicity, and are low resistance, And inqu wholeheartedly in order to obtain the component which has high dielectric breakdown voltage, and a semi-conductor ized agent is added in the range of 0.22 - 0.35 mol%. And the thing for which manganese, a silicon dioxide, and the titanium oxide for an excess are blended as shown in Table 1 and 2, and the thing of mean particle diameter which w described to Table 3 and 4 is used further, While raising and covering with the melting point of the constituent obtain by moreover permuting barium by coincidence by strontium and cull USHIMU and being able to avoid a reaction an welding with powder, it found out that the reduction in resistance and high dielectric-breakdown-voltage-ization wer attained.

[0043] That is, it is the total quantity of 0.05 - 0.10 mol%, a silicon dioxide, and the titanium oxide for an excess abo a manganese compound. 1.5-3.2 It blends so that it may become 0.3-2.3-mol% of within the limits, and the content o mol% and the above-mentioned silicon dioxide is the strontium of 1 - 10 mol%, and calcium of 13 - 18 mol% about barium further. It permutes by coincidence. Further the mean particle diameter of a barium carbonate 0.5-1.4 The thi of mum, and the mean particle diameter of titanium oxide Mean particle diameter 0.5-1.1 The thing of mum is used. Moreover, An organic system dispersant anionic to the time of mixing with the above-mentioned main raw material and other combination constituents is 0.05-0.8. The effectiveness that it is mixable to homogeneity while avoiding those condensation for each particle raw material by doing weight % use of is fully demonstrated. Moreover, dielectr breakdown voltage became possible [obtaining a practically required 35v //mm / or more PTC component] by low resistance at the time of a room temperature.

[0044] Consequently, the configuration of the above-mentioned example can produce the component which has high dielectric breakdown voltage by low resistance to the same rated voltage, and since the control to a big load is possib it can use it suitable for the current-limiting component in the circuit centering on a low-battery drive, i.e., the circuit element for overcurrent protections. Moreover, the above-mentioned configuration can be used suitable also for the circuit element for motor starting, a constant temperature heater element, and the component for demagnetization circuits.

[0045] Moreover, in comparison with the PTC component which has the same resistance, by having high dielectric breakdown voltage, conventionally, small and since-izing can be carried out [thin shape], the heating cost metallurg mold cost at the time of baking can be mitigated, a still cheaper manufacturing cost can be realized, and space-saving ization can be attained.

[0046] Moreover, since it does not contain the lead which has toxicity, that waste treatment becomes simple etc. has very high utility value on industry, and is useful while the above-mentioned configuration can avoid degradation of t manufacture environment by lead. In addition, what is necessary is not to be limited especially above, to satisfy a hig grade, although the example was given using a carbonate and an oxide as a start raw material, and just to use the raw

material which gives a predetermined component ratio by a pyrolysis etc. at the time of baking with the configuratio of the above-mentioned example.
[0047] Thus, when a raw material is mixed, by adding an anionic organic system dispersant, each raw material can b mixed to homogeneity as a particle. If a raw material is made into a particle, by being easy to condense each raw material, and adding the above-mentioned organic system dispersant, although the former was impossible for attainin mixing a particle to homogeneity, this can carry out amalgam decomposition of each above-mentioned particle, and mix it to homogeneity in the phase of the primary particle of particle original.
[0048] Thus, the compound currently mixed to homogeneity is dominance in respect of the reactivity in baking, or sintered density, and is reflecting the property of a semi-conductor with sufficient repeatability also in an electrical property. As for the addition of such an anionic organic system dispersant, using in 0.05 - 0.8 wt% is desirable. If the are too many the additions, it will condense on the contrary, and if too conversely few, a good dispersion effect is no shown.
[0049] In addition, although a dispersion effect is shown even if it is the organic system dispersant of the Nonion nature, the dispersion effect over the raw material of a particle is small compared with an anionic thing. In a cationic organic system dispersant, condensation is given conversely.
[0050] Moreover, although the example which used the thing of the polyvinyl alcohol system of a drainage system a binder was given in the above-mentioned example, styrene resin, and what neutralized the copolymer of a maleic anhydride with ammonia and acrylic resin can also be used.
[0051] Next, the measuring method of many physical properties of each above-mentioned sample is explained.
(1) The test portion of a resistance temperature characteristic was attached in the sample electrode holder for measurement, it equipped in the measurement tub (the Tabai Espec Corp. make, MINI-SUBZERO MC-810P), and change of the electric resistance of the sample to the temperature change to -50 - 180 ** was measured using the dire current-resistance meter (product made from YHP, and multimeter 3878A). Furthermore, change of the electric resistance in the temperature more than 180 ** was changed to another measurement tub (the product made from the Yamato science, and DX-30) the whole sample electrode holder, and measured the terminal from the above-mention measurement tub with the direct-current-resistance plan same as the above. The Curie point (Tc) of a sample plotted measured value from each above-mentioned measurement tub, and was computed as temperature which showed twic as many specific resistance as the minimum specific resistance.
[0052] (2) In the 25-degree C measurement tub, electric resistance was measured for the room temperature specific resistance sample using the above-mentioned direct-current-resistance meter. In preparation of the above-mentioned sample, the magnitude (a path and thickness) of a sample is measured before electrode formation, specific resistance (rho) was computed by the degree type, and this was made into specific resistance.
[0053] Rho=R-S/trho: Specific resistance [Omega-cm]
R: Measured value of electric resistance [omega]
S: Area of an electrode [cm2]
t: Thickness of a sample [cm]
(3) The dielectric-breakdown-voltage sample was attached in the electrode holder for measurement, and the direct-current regulated power supply (the product made from TAKASAGO LTD, GPO 25-5, and GPO 350-2), and a direc current-voltage meter (HEWLETT PACKARD make and 3457A) and a multimeter (ADVANTEST make) were connected. When raising gradually the electrical potential difference impressed to the above-mentioned sample from 100mV, the electrical potential difference which a current value increases rapidly and begins a thermal run away was made into the dielectric breakdown voltage of the above-mentioned sample.
[0054]
[Effect of the Invention] The barium titanate system semi-conductor porcelain constituent of this invention is a mean diameter as mentioned above. 0.5-1.4 Barium-carbonate powder of mum, and mean diameter 0.5-1.1 It is the configuration which the titanium oxide powder of mum was used as a main raw material, and the above-mentioned barium-carbonate powder and titanium oxide powder were mixed, and was calcinated under the oxidizing atmospher
[0055] So, since dielectric breakdown voltage can be made high while being able to make small specific resistance a the time of a room temperature, the above-mentioned configuration can produce the component which has high dielectric breakdown voltage by low resistance to the same rated voltage, and since the control to a big load is possib it can use it suitable for the current-limiting component in the circuit centering on a low-battery drive.
[0056] Moreover, in comparison with the PTC component which has the same resistance, by having high dielectric breakdown voltage, conventionally, small and since-izing can be carried out [thin shape], the heating cost metallurg mold cost at the time of baking can be mitigated, and a still cheaper manufacturing cost can be realized.
[0057] Moreover, since the above-mentioned configuration does not contain the lead which has toxicity, it does so th effectiveness that that waste treatment becomes simple etc. has the very high utility value on industry, and is useful while it can avoid degradation of the manufacture environment by lead.

[0058] The manufacture approach of the barium titanate system semi-conductor porcelain constituent of this inventio is an approach which an anionic organic system dispersant is added as mentioned above to the combination constitue which uses barium-carbonate powder and titanium oxide powder as a principal component, and the above-mentioned combination constituent is mixed, and is calcinated under an oxidizing atmosphere.

[0059] So, by the above-mentioned approach, when a combination constituent is mixed, the effectiveness that the barium titanate system semi-conductor porcelain constituent which has the property indicated in the effectiveness of configuration according to claim 1 can be obtained to stability is done by adding an anionic organic system dispersan

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[Translation done.]